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in Kraft Mills Using Headspace Gas Chromatography

J.Y. Zhu, X.-S. Chai, and B. Dhasmana

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Development of a Database for VOC Emission Prediction in Kraft Mills Using Headspace Gas Chromatography

Junyong Zhu, Xin-Sheng Chai, and Bindu Dhasmana

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, GA 30318, USA
(404) 894-5310 (404) 894-4778 (Fax)

ABSTRACT

VOC emission in kraft mills has been an environmental concern. The VOC content and the vapor-liquid phase equilibrium are the two factors that dictate VOC emission. The present study reports the development of analytical methods and a protocol to develop a database that describes the contents and the VLE behaviors of VOC's in various kraft mill streams using commercial headspace gas chromatography. The methods are indirect, rapid, automated, and do not require modification of the sample matrix. Validation experiments with VOC-water mixtures indicate that the methods are accurate. Preliminary results of various mill streams are also obtained using the developed protocol.

INTRODUCTION

The new toxic and permit provisions of the 1990 clean air amendments require information on emissions of volatile organic compounds (VOC's) from pulp and paper mill sources. Many VOC's are now on the list of hazardous air pollutants. Several studies on VOC emissions at kraft mills have been conducted. Venketesh et al. [1] reported a millwide VOC prediction using a process simulation technique. The National Council of the Paper Industry for Air and Stream Improvement (NCASI) conducted a series of studies on VOC emissions at kraft mills. NCASI's studies [2] indicated that the VOC content and the thermodynamic vapor-liquid phase equilibrium behavior of VOC's are two of the key factors that affect the release of VOC's during mill operations. Therefore, a database that quantifies the contents and the VLE behaviors of VOC's in kraft mill streams is very important for understanding VOC emissions and emission predictions using computer simulation models [3]. Unfortunately, limited experimental techniques are available for the determination of the contents and VLE behaviors of VOC's in kraft mill streams due to their corrosive nature.

Recently, Gunshefki and Cloutier [4] developed a method for measuring methanol contents in black liquor. However, the method involves a series of sample pretreatment. It is, therefore, very complicated, time-consuming, and less accurate. There are many methods available to study vapor-liquid phase equilibrium [5-7]; however, most available methods are complicated to implement and involve calibration. Much research on vapor-liquid phase equilibrium has been conducted using headspace (HS) GC systems [8-12] that provide direct vapor phase analysis. However, traditional HSGC methods require the direct analysis of solute content in the sample stream, not suitable for mill stream VLE studies. Furthermore, most of the existing indirect HSGC methods have either practical difficulties to implement or complicated calibration procedures.

In this study, we report on the development of indirect methods for rapid, automated, and precise determination of the contents and the vapor-liquid phase equilibrium partitioning of VOC's in kraft mill streams using a commercial headspace gas

chromatography system. The detail protocols for these measurements and the applications for the mill samples are also presented.

METHODOLOGY

Quantification of VOC Contents [13].

The method is schematically described in Fig. 1. We use two sample vials filled with the same volume of sample solution. We then add a small amount of concentrated solution of known concentration into one of the vials. After a phase equilibrium is established within each vial, we conduct headspace GC analysis for each sample vial. Because of a very low concentration, the solute VLE partitioning coefficients in these two vials agree with Henry's Law, i.e.,

$$H_c = \frac{C_g^1}{C_1} = \frac{C_g^2}{C_2} \quad (1)$$

where C_i and C_g^i are the solute concentrations in the liquid and vapor phases at equilibrium in vial i , respectively.

The amount of solutes in the vapor phase at equilibrium state in these two vials can be described as:

$$C_g^1 V_g^0 = C_0 V_l^0 - C_1 V_l^0, \quad (2)$$

and

$$C_g^2 V_g^0 = C_0 V_l^0 + C_s V_s - C_2 V_l^0, \quad (3)$$

where C_0 and C_s are the concentrations of the solute in the sample and in the standard solution, respectively. The V_l^0 , V_s , and V_g^0 are the volumes of the sample, standard solution, and headspace, respectively.

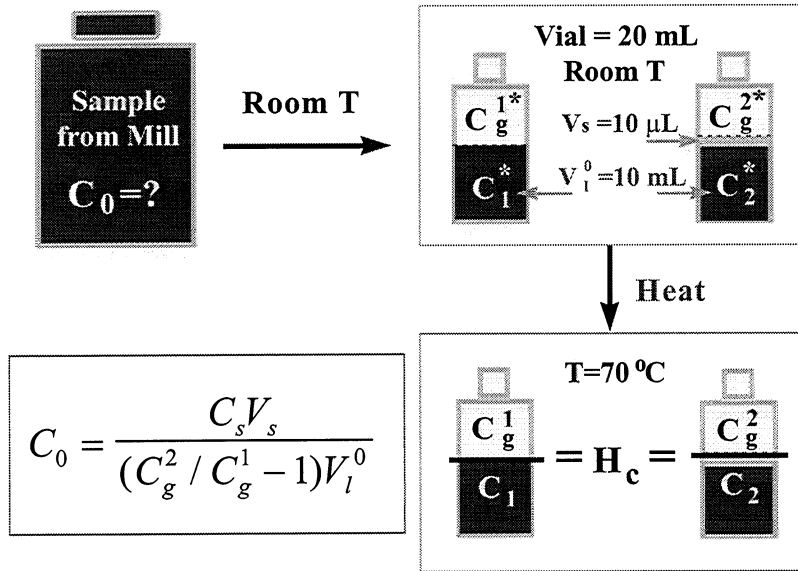


Fig. 1. Schematic diagram describing the present indirect HSGC method for VOC content measurements.

We can derive the initial solute concentration in the sample solution from Eqns. (2) and (3),

$$C_0 = \frac{C_s V_s}{(C_g^2 / C_g^1 - 1) V_l^0}, \quad (4)$$

where we assume that the total volume of the solution in the vials remains the same because of $V_l^0 \gg V_s$.

The ratio of the solute concentration in the vapor, C_g^2 / C_g^1 , is proportional to the ratio of the peak areas, A_2 and A_1 , measured from GC analysis. Thus, we can rewrite Eqn. (4) as,

$$C_0 = \frac{C_s V_s}{(A_2 / A_1 - 1) V_l^0}. \quad (5)$$

Determination of VOC Henry's Constant [14].

The indirect HSGC method for measuring VLE Henry's constant is schematically shown in Fig. 2. We used two vials filled with the same sample solution but significant

volume difference. We then conducted headspace GC analysis for each vial when the phase equilibrium was established within the vials. Because the two vials contain the same dilute solution, the solute VLE partitioning coefficients in these two vials agree with Henry's Law as shown in Eqn. (1). We can express the total moles, M , of the solute in these two vials as follows,

$$M_1 = C_l^0 V_l^1 = C_l^1 V_l^1 + C_g^1 V_g^1 = C_g^1 \left[(V_l^1 / H_c) + V_g^1 \right], \quad (6)$$

and

$$M_2 = C_l^0 V_l^2 = C_l^2 V_l^2 + C_g^2 V_g^2 = C_g^2 \left[(V_l^2 / H_c) + V_g^2 \right], \quad (7)$$

where C_g is the concentration of solute in the vapor phase, and V_g is the vapor volume in the vial.

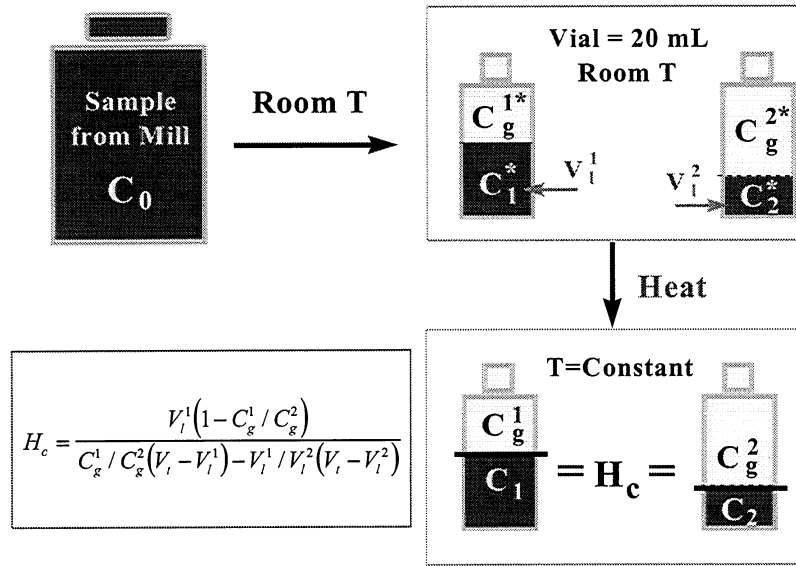


Fig. 2. Schematic diagram describing the present indirect HSGC method for VLE partitioning Henry's constant measurements.

We can derive the dimensionless Henry's constant H_c from Eqns. (6) and (7),

$$H_c = \frac{V_l^1 (1 - C_g^1 / C_g^2)}{C_g^1 / C_g^2 (V_l - V_l^1) - V_l^1 / V_l^2 (V_l - V_l^2)} = \frac{V_l^1 (1 - A_1 / A_2)}{A_1 / A_2 (V_l - V_l^1) - V_l^1 / V_l^2 (V_l - V_l^2)} \quad (8)$$

MEASUREMENT PROTOCOLS

I. Liquid VOC Content Measurement.

This measurement protocol is used to simultaneously determine liquid contents of methanol, MEK, and acetone in sample solution.

Apparatus

1. A gas chromatograph, HP 6890 (Hewlett-Packard) equipped with a single or dual column instrument with flame ionization detector (FID). A HP-5 capillary column (Hewlett-Packard) operated at 30°C with an injection port temperature of 250°C and a detector temperature of 250°C is used for species separation. GC conditions: helium carrier gas flow rate: 3.8 ml/min, and hydrogen gas and compress air flow rates for the FID: 35 and 400 ml/min, respectively.

2. An automatic Headspace Sampler, HP-7694 (Hewlett-Packard). Headspace conditions: thermo equilibration time 25 min with gentle shaking, injection time: 1.0 min, vial pressurization time: 0.3-0.5 min, and sample loop fill time: 0.2 min. In headspace sampling, the solid, liquid, or gaseous sample is placed in a vial and sealed by a septum with a crimper. The sampling operation is controlled by a personal computer and automated.

3. Miscellaneous: volumetric flask, pipettes, 10 µl microsyringe, 20-ml vials.

Reagents

Standard mix solvent of methanol, acetone, and MEK. Preparation: Add about 9 ml of methanol into a 10-ml dried volumetric flask. Pipette 0.1 ml of MEK and 0.1 ml of Acetone into the volumetric flask, respectively, then fill methanol to the mark of 10 ml of the flask. The volume of the headspace in the volumetric flask should be as small as possible to avoid the vaporization of the solutes from the solvent. The concentrations of methanol, acetone, and MEK are 24.5, 0.135, and 0.111 mole/L, respectively.

Procedure

1. Pipette 10 ml of sample solution into three 20-ml vials, then close the vials.
2. Pipette 10 ml of sample solution into another three 20-ml vials. Add 10 µl of standard solvent by microsyringe into each vial, then close the vial.
3. Put the vials into the headspace Sampler for equilibration and then measure by the GC.

4. Triplicate run the samples in step 1, determine the peak areas at retention times of 2.24, 2.50, and 3.23 min for methanol, acetone, and MEK, respectively. Then calculate the average peak areas $\bar{A}_{1,MeOH}$, $\bar{A}_{1,acetone}$, and $\bar{A}_{1,MEK}$.
5. Triplicate run the samples in step 2, determine the peak areas at retention times of 2.24, 2.50, and 3.23 min for methanol, acetone, and MEK, respectively. Then calculate the average peak areas $\bar{A}_{2,MeOH}$, $\bar{A}_{2,acetone}$ and $\bar{A}_{2,MEK}$.

Calculation

Use the following equation to calculate the concentrations:

$$C_{0,i} = \frac{C_{s,i} V_s}{(\bar{A}_{2,i} / \bar{A}_{1,i} - 1) V_l^0}$$

where $C_{0,i}$, $C_{s,i}$ and V_l^0 , V_s are i component concentrations and the volumes of the original testing sample and the standard solution in mole/L, respectively; $\bar{A}_{1,i}$ and $\bar{A}_{2,i}$ are the averaged GC peak areas of component i in the vapor phase measured before and after standard addition, respectively.

II. VLE Measurement.

This protocol is used to determine Henry's constant of VOC's in the sample solution.

Apparatus

The system and operating conditions of gas chromatography are the same as that mentioned in *Protocol I*. The operating conditions of the headspace Sampler are also the same as above, except the time of equilibration will be determined by the sample volume used in the experiment. The suggested sample volumes (a and b) and equilibrium time in the headspace Sampler are listed in Table I.

Procedure

1. Pipette a ml of sample solution into three 20-ml vials, then close the vials.
2. Pipette b ml of sample solution into another three 20-ml vials, then close the vials.
3. Put the vials into the Headspace Sampler for equilibration and then measure by the GC.

4. Triplicate run the samples in step 1, determine the peak area at the retention time of the solute as indicated in *Protocol I*. Then calculate the average peak areas $\bar{A}_{1,i}$.
5. Triplicate run the samples in step 2, determine the peak areas at the retention time of the solute. Then calculate the average peak areas $\bar{A}_{2,i}$.

Table I. Suggested sample volumes and equilibration time in headspace sampler.

Henry's constant	V_1 , ml	V_2 , ml	Equilibration time*, min.
0.001	0.1	0.01	5
0.01	1	0.1	15
0.1	10	1	25
1	10	5	25
10	10	7	25
100	10	9	25

*For the samples with humic matters or particles, HSGC analysis should be conducted immediately after adding sample solution into the vial.

Calculation

Use the following equation to calculate results:

$$H_c = \frac{V_1(1 - \bar{A}_{1,i} / \bar{A}_{2,i})}{\bar{A}_{1,i} / \bar{A}_{2,i}(V_t - V_1) - V_1 / V_2(V_t - V_2)}$$

where H_c is the Henry's law constant (dimensionless). $\bar{A}_{1,i}$, $\bar{A}_{2,i}$ and V_1 , V_2 are the average GC peak area of the i component measured and the sample volume (in ml) in vial 1 and 2, respectively.

APPLICATIONS

Measurement of Liquid VOC Contents in Mill Streams.

Methanol, acetone, and MEK are the major VOC species with lower boiling points in most mill streams. Traditional methods to measure these VOC's use organic solvents to extract them from the aqueous phase. These methods are time-consuming and less accurate due to a low concentration of these species in mill streams. With the present method (Protocol I), we can measure methanol, acetone, and MEK in various mill streams

simultaneously. The measurements are rapid, automated, and accurate as demonstrated in a previous study [13]. Some results of VOC contents in various streams of a kraft mill are shown in Table II.

Measurement of Methanol Henry's Constant in Black Liquors.

It is known that 90 % of VOC's in mill streams is methanol. It is therefore important to understand methanol's thermodynamic behavior in these mill streams. The measurement of methanol Henry's constant in mill streams is also very difficult because it is very small. We can use the present method (Protocols II) to measure the Henry's constant of methanol in mill streams with a reasonable accuracy.

Both softwood and hardwood black liquor samples from a mill were used in this study. Fig. 3 shows the effect of temperature on the methanol Henry's constant in black liquors along with the data obtained in the methanol-water mixture. The results indicate that the logarithm of Henry's constant in the two black liquor samples decreases linearly with the inverse of temperature. The variation in the measured Henry's constant among these three types of samples is very significant. We believe that the significant variations in the composition, ionic strength, solid contents, etc., among these samples, may cause the large variation in the Henry's constant. We will conduct a detailed study to understand the effect of various parameters on the Henry's constant in the future.

CONCLUSIONS

The present study reported on the methods and protocols to measure the contents and the vapor-liquid phase equilibrium partitioning coefficients of VOC's in mill streams using a commercial headspace gas chromatography system. Both methods are rapid, automated, accurate, and do not require calibration and modification of the sample matrix and can also be easily applied to various industrial and environmental streams. Preliminary measurements of VOC content and Henry's constant of methanol in kraft mill streams using the methods developed were conducted.

Table II. VOC contents measured in various streams from a pulp mill.

Sample Location Description	Label	MeOH	Acetone	MEK
		(ppm)	(ppb)	(ppb)
1 st stage showers, 2 nd stage filtrate	No. 1 Washer	209.5	494	406
	No. 2 Washer	275.0	484	394
2 nd stage showers, 1 st stage filtrate	No. 1 Washer	149.8	980	439
	No. 2 Washer	312.7	852	511
3 rd stage showers	No. 1 Washer	122.6	683	452
	No. 2 Washer	203.8	715	526
side combined condensate (blow recovery)	No. 1 Washer	178.6	1327	592
	No. 2 Washer	382.6	1113	774
1 st stage filtrate	No. 2 Washer	349.0	520	270
3 rd stage filtrate	No. 1 Washer	332.2	930	564
combined weak black liquor to recovery		292.4	670	315
evaporator seal tank condensate	No. 2 (M24-0542)	93.1	762	665
	No. 2 (24-0529)	673.1	4138	425
evaporator clean condensate	No. 3	2.0	-	31
	No. 3 (24-0509)	1.7	-	231
evaporator	No. 2	27.1	-	218
evaporator seal tank	No. 1 (M24-0027)	3954.4	11	2706
combined condensate of hotwell	No. 3	659.1	16067	7826
paper-machine condensate	No. 1	3.3	-	59
	No. 2 & No. 3	3.5	-	124
top headbox	No. 1	57.4	323	108
	No. 2	55.3	260	129
base headbox	No. 1	88.8	433	167
	No. 2	64.9	315	158
headbox	No. 3	46.8	-	-
wire pit	No. 1	86.5	375	141
	No. 2	91.8	508	129
	No. 3	90.9	-	-
water reclaim sump	No. 1	13.0	192	62
vacuum dump	No. 2	20.6	-	-
side hill screen drain off	No. 3	65.7	-	-

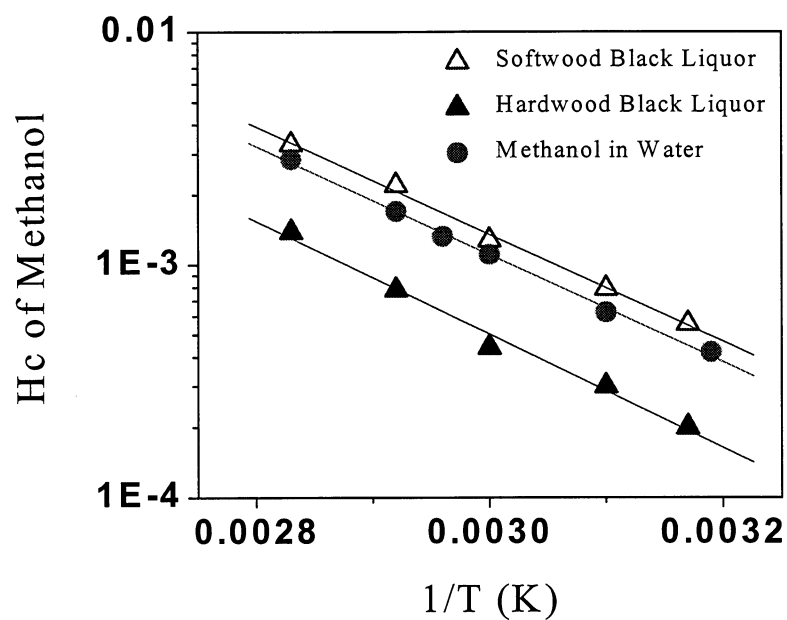


Fig. 3. Measured methanol Henry's constant in two black liquor samples.

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